Summary

1. Measurements of the cells Ag | AgCl | HCl (m_2) | HCl (m_1) | AgCl | Ag at 25° with alcohol and 50 mole per cent. alcohol-water mixtures have been presented.

2. By the method employed by MacInnes and Beattie the cation transference numbers in these solutions have been calculated.

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[CONTRIBUTION FROM THE PHYSICAL AND CHEMICAL LABORATORIES OF THE UNIVERSITY OF MISSOURI]

LUMINESCENCE OF GRIGNARD COMPOUNDS: SPECTRA AND BRIGHTNESS

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In a previous article,[1] the authors reported the results of a rather extended investigation of the luminescence of compounds of the type RMgX, where R is an organic radical and X a halogen. The effect of several factors on the color and on the brightness of the luminescence was discussed. It was shown that, in order to obtain light from these compounds in ether solution, on oxidation with oxygen, it is necessary for the magnesium to be attached directly to an unsaturated carbon atom in R.

It is the purpose of the present article to record observations of a few new compounds, to describe work on the spectra of the luminescence, and to give the results of an attempt to secure quantitative measurements of the brightness of the chemiluminescence.

Extension of Previous Investigations

One of the factors discussed in the previous article referred to, is the nature of the oxidizing agent used. It was shown that while benzene triozonide had been reported as giving some light, the only other oxidizing agent of any importance is oxygen, which is much more effective than anything else tried. Certain organic peroxides, however, are found to give some light. The writers are indebted to Professor Henry Gilman of the University of Iowa for the information that benzoyl peroxide, ethyl peroxide, and diacetone peroxide, give light. Tests show, however, at least with benzoyl peroxide, that the light so obtained is faint compared with that from oxygen. The tests were made on such representative compounds as C_6H_5MgBr, p-BrC_6H_4MgBr and p-ClC_6H_4MgBr.

The question of obtaining light from compounds containing other metals than magnesium was also discussed in the article referred to. Zinc compounds were shown not to be luminescent and mercury compounds were also so reported. The work on the mercury compounds has been

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[1] Dufford, Calvert and Nightingale, THIS JOURNAL, **45**, 2058 (1923).

repeated and extended, including the compound p-$CH_3C_6H_4HgBr$. No light was obtained from any mercury compound tried. However, the compound C_6H_5CaI was prepared, and was found to give a yellowish light on oxidation; but the light is not very bright, perhaps as bright as from C_6H_5MgI. No light was obtained from this compound with chloropicrin. The compound C_2H_5CaI was also prepared, but gave no light.

One of the most interesting factors studied is the effect of the "loading" groups substituted in the benzene ring, but not directly concerned in the reaction. It was shown in the earlier article that in the series p-IC_6H_4MgBr, p-BrC_6H_4MgBr, p-ClC_6H_4MgBr, where the loading groups are iodine, bromine and chlorine, respectively, both the brightness and the effective wave length increase progressively from iodine to chlorine. It seemed desirable to see whether the effect would be carried still further in the compound p-FC_6H_4MgBr. It is a surprising fact that it is not. The accompanying photograph (Fig. 1), on comparison with Figs. 3 D and 4 D, of the earlier article, will show the effect. The light from this compound is much fainter than that from p-ClC_6H_4MgBr, fainter even than the light from p-BrC_6H_4MgBr. Moreover, its effective wave length is shorter than that of any other compound in the series, for the light is deep violet-blue. This unexpected behavior gives added verification, in striking fashion, of the fact that the mass of the loading group appears not to control either the brightness or the color of the luminescence.

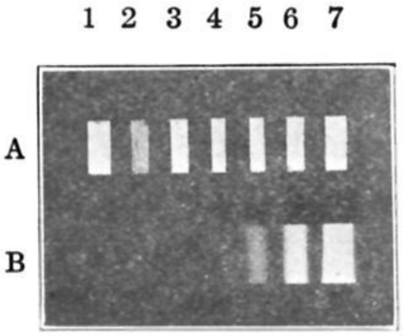

Fig. 1.—Luminescence of Grignard compound, p-FC_6H_4MgBr. A, white light. B, luminescence.

Efforts to prepare the compound C_6H_5MgF were not successful, so that it is not yet possible to say whether it will fit in with the series of monohalogen Grignard compounds discussed in the previous article.

Some new naphthalene compounds were studied; α-$C_{10}H_7MgI$ gives a faint light, and β-$C_{10}H_7MgI$ gives a fair light, observable visually through Filters 3, 4, 5 and 6.

The behavior of the β-naphthalene compounds, which radiate so much more brightly than the alpha compounds, suggested the possibility of studying the effect of doubly loading the benzene ring. An observation found on record, that $(1,2)(CH_3)_2C_6H_3MgBr$ (4) gives a bright light, seemed to indicate that this compound might be analogous to the β-naphthalene Grignard compounds, as suggested in the previous article. Hence, several derivatives of the xylenes and related compounds were studied. These compounds are rather disappointing, in that none of them is remarkably bright. The brightness of $(1,2)(CH_3)_2C_6H_3MgBr$ (4) is rather less than published statements would lead one to expect, and is less than that of p-

$CH_3C_6H_4MgBr$. The compounds $(1,4)(CH_3)_2C_6H_3MgBr$ (3) and $(1,3)(CH_3)_2C_6H_3MgBr$ (4) are still fainter. The compound from 2-bromocymene is barely brighter than the second of the xylene compounds just mentioned. If the expected analogy with the naphthalenes held, the compound $(1,2)$-$ClCH_3C_6H_3MgBr$ (4) would be brighter than *p*-ClC_6H_4MgBr; but instead, it is unmistakably fainter. Apparently, the analogy fails in every case tried; and doubly-loaded benzene rings are generally less strongly luminescent than the corresponding singly-loaded compounds.

All the compounds studied appear to confirm the rule that the magnesium must be attached directly to an unsaturated carbon atom in order to give light in ether solution. The Grignard compound from 9,10-dibromo-anthracene, previously described, might appear to be an exception, but the fact that it is luminescent might be considered as evidence that the 9,10-carbon atoms in anthracene are in much the same condition as the carbon atoms in benzene and therefore unsaturated.

An attempt to detect possible ultraviolet radiation from aliphatic Grignard compounds, by oxidizing them in quartz test-tubes held close to a photographic plate, gave negative results. Hence, it appears that if these compounds radiate on oxidation, the radiation must be in the infra-red. This does not exclude the possibility, of course, that some other method of oxidation with oxygen might make them give out light. When the oxidation is allowed to proceed rapidly, the material becomes very hot and a faint glow appears, followed in a second or two by a violent explosion. This glow appears to be due to the combustion of the ether, and is probably not due to the Grignard compound at all.

The fluorescence shown in ultraviolet light by the oxidation products of these Grignard compounds has been studied further. The most salient facts regarding *p*-BrC_6H_4MgBr have already been published.[2] It may be stated that all the halogen derivatives of benzene behave similarly, showing both single-banded and multiple-banded fluorescence spectra. Naphthalene derivatives uniformly give single-banded fluorescence spectra.

By means of an improvised spectrograph of special construction, the writers have succeeded in obtaining direct spectrum photographs of the chemiluminescence of several of these compounds, as well as of the fluorescence of the oxidation products. The outstandingly bright compound of this type is *p*-ClC_6H_4MgBr, previously described by the writers. The two spectra for this compound are shown in Figs. 2 and 3. They will serve to verify the earlier statement by the writers that the two radiations are not identical, and to show that it is not quite exact to say, as certain writers[3] have stated, that "the difference is at most slight." The chemiluminescence spectra are always single-banded. Several other such spectra and a

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[2] Evans and Dufford, THIS JOURNAL, **45,** 278 (1923).

[3] Kautsky and Zocher, *Z. Elektrochem.*, **29,** 308 (1923).

description of the instrument used to obtain them, can be found in a recent article in the *Journal of the Optical Society of America* for October, 1924.

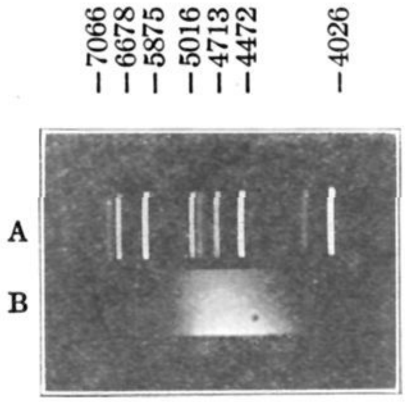

Fig. 2.—A, spectrum of helium; B, direct spectrum photograph of chemiluminescence of p-ClC_6H_4MgBr.

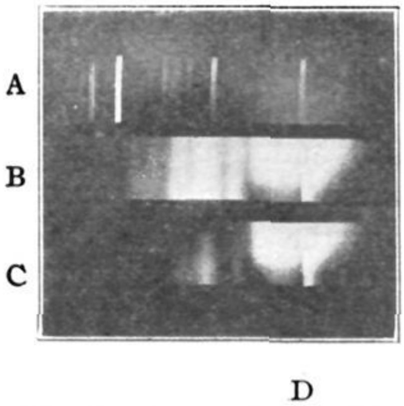

Fig. 3.—A, spectrum of helium; B, spectrum of fluorescence of oxidation product of p-ClC_6H_4MgBr; C, spectrum of fluorescence of oxidation product of p-BrC_6H_4MgBr. The band marked D is the exciting light.

No other such chemiluminescence spectra appear to have been obtained previously.

Table I summarizes for reference the facts concerning some compounds not already mentioned in the literature as luminescent. These compounds were of course specially selected as of interest in connection with others already studied; the number is small, for the desired compounds become more difficult to prepare as the investigation progresses.

Table I

Additional Luminescent Compounds

Compound	Chemiluminescence with oxygen Brightness	Color	Fluorescence of oxidation product
C_6H_5CaI	faint	yellowish	faint
p-FC_6H_4MgBr	bright	violet-blue	bright blue
$(1,2)ClCH_3C_6H_3(4)MgBr$	bright	blue	weak, dark green
2-$C_{10}H_{13}MgBr$ (cymene)	faint		faint
α-$C_{10}H_7MgI$	faint		faint
β-$C_{10}H_7MgI$	fair	deep blue	faint

Observations on Brightness of Luminescence

The brightness of such a source as the chemiluminescent reactions described in this article is, of course, greatly affected by the experimental conditions, and it is therefore necessary to adopt some advantageous set of conditions and duplicate them as closely as possible for each measurement in order to obtain comparable results from different compounds. In the present work the substances were put into small porcelain evaporatingdishes, with the solution about 1 cm. deep, and a jet of oxygen was blown upon the surface. This gives a small, bright spot where the jet strikes, upon which it is possible to make consistent observations. A series of observations on such a spot will show clearly the decrease in intensity with time; and a number of such series will give a fair idea of the brightness involved. Naturally, the most interesting question is the maximum brightness obtainable from a given compound. This is given in Table II, for some 25 compounds.

For crude observations on brightness, one may compare a reaction with some other reaction used as a standard; this was done in early work by the writers. Another method useful for very faint reactions is the comparison with a set of radio-luminous disks of known brightness. This method is of low accuracy, and the disks change slowly in brightness so that they must be recalibrated at intervals. A method described by Ives[4] is probably more accurate.

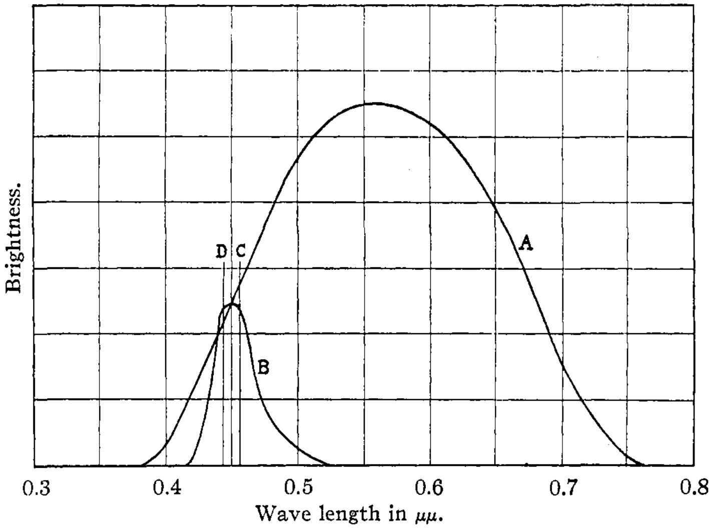

Fig. 4.

Nichols[5] has described a method that is by far the most convenient that has come to the attention of the writers. This method uses an optical pyrometer of the disappearing filament type, with a color screen in the eyepiece selected to give an approximate color match with the luminescence to be observed. It is obvious, however, from simple considerations, that this method is essentially inaccurate in case the spectral distribution of energy in the luminescence differs much from that of white light, as is

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[4] Ives, *J. Franklin Inst.*, **194**, 213 (1923).

[5] E. L. Nichols, *Science*, **55**, 157 (1922).

notably the case with those radiations where the most readily visible yellow light is almost completely absent. For example, let the apparent brightness (energy radiated multiplied by a visibility factor) be plotted as a function of the wave length, for a given source. If the source is a hot "black body," emitting white light, the curve will have a form somewhat like Curve A, of Fig. 4; but if the source is a luminescent body not radiating white light, the curve will probably have some such shape as Curve B. Now if the range of transmission of the eyepiece filter is CD, by the pyrometer method the curve A will be adjusted to have the same average height as B in the region CD. But since the areas under the two curves are proportional to the total brightness for all wave lengths, it is obvious that the pyrometer will always overestimate the total brightness of the luminescence. While it is occasionally useful to know the brightness at the wave length of maximum emission, the above considerations led the writers to abandon the pyrometer method except for comparing sources very similar in spectral distribution. As an example of this effect, Nichols reports the brightness of the light from Harvey's luciferin, the material obtained from the small crustacean *cypridina*, as about 18 millilamberts; while the writers, using the photometer method described below, on a sample of luciferin kindly supplied by Professor Harvey, were not able to observe more than about 2 millilamberts. While no doubt the experimental conditions may have been different, it seems very likely that the chief reason for this discrepancy lies in the error inherent in the pyrometer method. The light from luciferin is a bright blue, and its spectral distribution is very different from that of white light. It is hoped that further work to check this matter can be carried out later.

Several types of photometer have been described for low intensity work, but for various reasons none of these seemed available for the work in hand. The writers therefore finally designed and built an instrument which did the work desired in satisfactory fashion. The instrument used had a double-barreled telescope, with the two barrels at nearly right angles, and with a small right-angled prism in the eyepiece, so that the two fields of view were seen as the two halves of a circle. One telescope was directed toward a variable secondary standard of brightness made of a lamp in a tight box with a ground-glass window having a blue-green monochromatic color filter behind it. The other telescope was directed toward the object to be measured, and the voltage on the variable standard adjusted to give an intensity match between the two halves of the field. Consistent readings, agreeing usually within 1 v. could be obtained. When these readings had been completed, the object was replaced by a variable primary standard, also made of a light in a tight box, with a colored window; this standard was calibrated for the writers by the Bureau of Standards, the brightness of the surface of the window being given as a function of the current through the lamp. The substitution of the primary standard for the object measured eliminates errors and corrections on account of different reflections and transmissions in the two barrels of the telescope. The unit of brightness used, the lambert, is the brightness of a perfectly diffusing and reflecting surface illuminated by a source of light emitting 1 candle power placed at a distance of 1 meter. It should be emphasized that the method just described uses all the light, of all wave lengths, given out by the luminescent body, and so avoids the error inherent in the pyrometer method. The colored windows on the standards aid in judging when an intensity match for the two halves of the field is obtained, since the colors are then nearly alike. Probably an instrument of the illuminometer type would have been nearly as satisfactory.

While the results of observations on different portions of a given sample of material agree very closely, the results from different samples made on different days are not always in so good agreement. There are a few values given in Table II, as for α-naphthylmagnesium bromide and for *o*-ClC_6H_4MgBr, that are almost certainly too low, as the result of samples less active than they should have been. This sort of variation appears to be rather characteristic of Grignard compounds. For the most part, however, the values given in the table are thought to be accurate to within 10%, and this is about all that could be expected under the circumstances. Many of the results have been confirmed approximately by the pyrometer method.

The results given show in striking fashion, for three different series, the enormously greater brightness of *para* substituted as compared with *ortho* or *meta* substituted benzene ring compounds. They show also that neither *ortho* nor *meta* compounds are consistently brighter than the other. The

TABLE II

BRIGHTNESS OF CHEMILUMINESCENCE

Grignard compound	Brightness in microlamberts	Grignard compound	Brightness in microlamberts
β-$C_6H_5CH{:}CHMgBr$	5.0	*m*-$CH_3C_6H_4MgBr$	31.0
C_6H_5MgI	2.5	*p*-$CH_3C_6H_4MgBr$	153
C_6H_5MgBr	13.0	$(1,2)(CH_3)_2C_6H_3(4)MgBr$	140
o-BrC_6H_4MgBr	43.0	$(1,4)(CH_3)_2C_6H_3(2)MgBr$	95
m-BrC_6H_4MgBr	43.0	$(1,2)ClCH_3C_6H_3(4)MgBr$	405
p-BrC_6H_4MgBr	1110	$(2)C_{10}H_{13}MgBr$	110
o-ClC_6H_4MgBr	14 (?)	α-$C_{10}H_7MgBr$	245 (?)
m-ClC_6H_4MgBr	205	β-$C_{10}H_7MgBr$	1110[a]
p-ClC_6H_4MgBr	2400	α-$C_{10}H_7MgI$	0.7
p-FC_6H_4MgBr	470	β-$C_{10}H_7MgI$	43.0
p-ClC_6H_4MgI	110	$(1,4)BrC_{10}H_6MgBr$	26.0
p-IC_6H_4MgBr	305	$(1,4)ClC_{10}H_6MgBr$	305
o-$CH_3C_6H_4MgBr$	66.0		

[a] By comparison with *p*-BrC_6H_4MgBr, using a pyrometer.

variation in brightness when the substituted halogen is varied, as in the dihalogen derivatives, is very well shown. Several other effects, described by the writers in the earlier article referred to,[1] are also brought out. With this quantitative evidence, it is difficult to see how anyone can claim that the mass of the reacting molecules has anything to do with the brightness of the radiation.

The writers are indebted to several of the members of the staff of the Nela Research Laboratory for helpful suggestions as to methods, and especially to the late director, Dr. E. F. Nichols, for encouragement to continue the work.

Summary

1. A number of organometallic halides have been examined for luminescence, and six are here reported as chemiluminescent; the relation of these compounds to others previously described is discussed.

2. It is shown that calcium may serve instead of the magnesium in chemiluminescent compounds.

3. Certain other oxidizing agents than oxygen are reported as giving light with these compounds.

4. Direct spectrum photographs of the chemiluminescence of several Grignard compounds have been obtained. That from *p*-ClC_6H_4MgBr is reproduced here, and is compared with the associated multiple-banded fluorescence spectrum.

5. Methods of measuring the brightness of very faint sources are discussed, and a type of photometer is described which was found useful for such work.

6. Observations are given on the brightness of some 25 of the most important of the chemiluminescent Grignard compounds. These measurements verify quantitatively the conclusions given by the writers in an earlier article.[1]

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